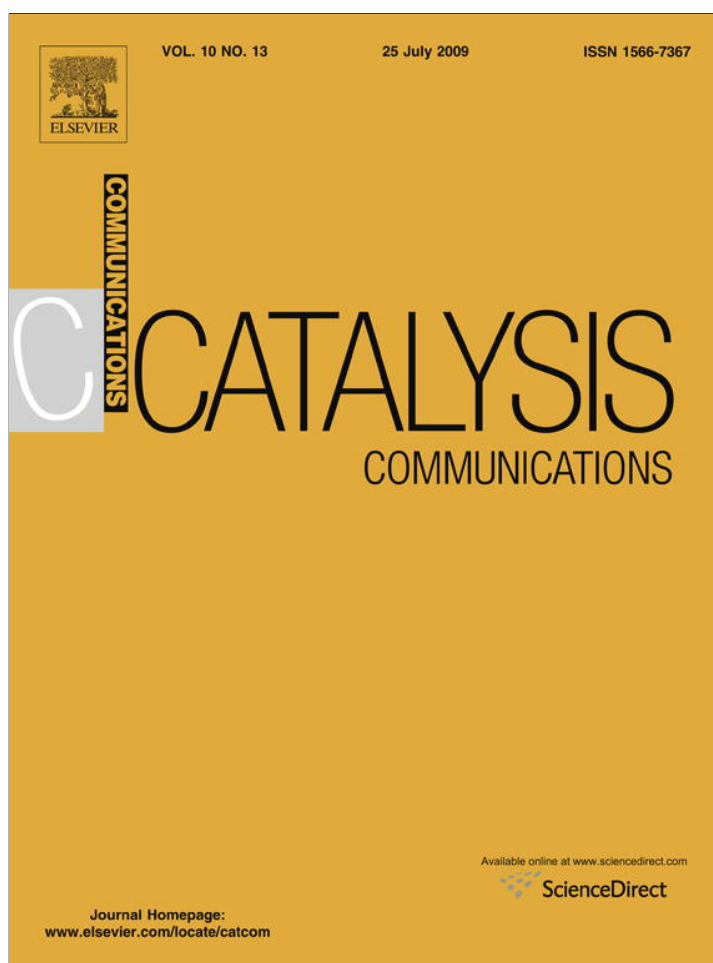


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# Palladium doped manganese dioxide catalysts for low temperature carbon monoxide oxidation

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## ABSTRACT

Nano-sized palladium doped manganese dioxide catalysts with varying compositions were prepared by the co-precipitation method. Palladium doped manganese dioxide catalysts show markedly enhanced CO oxidation activity, and CO conversion even at 35 °C. Strong interaction occurs between palladium and manganese dioxide which results in high catalytic activity and total CO conversion occurs at a lower temperature. Activity test carried out at fixed temperature indicate that the catalysts retain their activity with increasing time. The moisture influenced the catalytic activities considerably. The SEM study shows that particles are nano-sized and almost spherical in shape.

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## 1. Introduction

Carbon monoxide (CO) is one of the toxic components of industrial waste gases and exhaust gases from automobiles. It is also formed in the regeneration of hydrocarbon cracking catalysts. It causes potential harmful effects on living beings and environment. Thus complete elimination or abatement below the permissible levels fixed by environmental regulations is a major concern. In recent years many methods have been used to reduce the emissions of CO. The catalytic technologies are attractive because of their low cost and high efficiency. Nanotechnology has recently experienced a rapid escalation owing to the unique physical and chemical properties of nanoparticles compared with the bulk solids [1–4].

Many different catalysts have been prepared and tested for the low temperature carbon monoxide oxidation activity. Precious metals like Pt, Pd, Au, Rh, Ru are active catalyst for CO conversion [5–7]. They generally allow low operating temperatures and higher space velocities than the transition metal oxide based catalysts. However, due to the high cost of noble metals and their less availability as well as sublimation and sintering problems, considerable part of the research has been devoted to the development of suitable catalyst among the transition metal oxides [8–10]. Appropriate combination of oxides and some mixed metal oxides exhibit greater activity and thermal stability than the single oxides. Combination of noble metals with transition metal oxides result in materials with high catalytic activity, stability and also require less

quantity of the noble metals [11–14]. Few reports are available on palladium supported catalysts, indicating that they are very active and stable. Palladium is used as catalyst in various types of reactions [15–18]. Manganese dioxide is an important material widely used as a catalyst [19–22], cathodic material in batteries [23,24] and in organic synthesis. The properties of MnO<sub>2</sub> are influenced significantly by its structure, morphology and preparative methods. The basic building block of manganese oxide is MnO<sub>6</sub> octahedra, these octahedra share their corners or edges into variety of different structural arrangements [25,26]. A great deal of attention has been paid to the preparation of MnO<sub>2</sub> with different crystallographic structures and morphologies [25–28].

In the present investigation, a series of nano-sized Pd doped MnO<sub>2</sub> catalyst were prepared by dextrose aided co-precipitation technique. The prepared catalysts were tested for CO oxidation reaction and other studies. The interaction of Pd with MnO<sub>2</sub> results in a good catalytic activity. The effect of moisture was studied to see the performance of the catalyst for CO conversion along with activity test.

## 2. Experimental

### 2.1. Catalyst preparation

The solid catalysts of composition Mn<sub>1-x</sub>Pd<sub>x</sub>O<sub>2</sub> (where X = 0, 0.02, 0.05, 0.08) were prepared by dextrose aided co-precipitation technique. All reagents used were of analytical grade. Appropriate amount of manganese (II) acetate was dissolved in distilled water at room temperature, calculated amount of palladium (II) chloride

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was taken in a separate beaker, to this distilled water and concentrated nitric acid was added and heated with stirring to dissolve completely. Both these solutions were mixed together at room temperature to get a clear homogeneous solution. This solution was added to 2% dextrose solution at 100 °C with stirring, dextrose solution was added to avoid agglomeration. The precipitation was carried out by adding drop by drop solution of sodium hydroxide (10%) to the above solution under vigorous stirring. Subsequently, the suspension of precipitated metal hydroxide mixture (at pH 9) was subjected to oxidation by drop wise addition of 30% H<sub>2</sub>O<sub>2</sub> solution with constant stirring in order to adjust the appropriate oxidation state of the metal ions. The precipitate was then digested on a water bath for three hours, filtered and dried in air at 120 °C for 10 h. Finally the dried precipitate was homogenized well in mortar and calcined in air at 400 °C for 5 h.

## 2.2. Catalyst characterization

The X-ray powder diffraction (XRD) measurement was carried out on RIGAKU diffractometer, using Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature using a SMART SORB-91 surface area analyzer. The samples were degassed at 200 °C for 4 h prior to the adsorption experiments. The surface morphology was determined with JSM-5800LV scanning electron microscope (SEM) instrument operating at 20 kV. Thermal analysis was carried out on a NETZCH STA 409 PC TG/DSC instrument in air at a heating rate of 10 K min<sup>-1</sup> and heated from ambient to 1100 °C.

## 2.3. Catalytic activity

The catalytic tests for CO oxidation by O<sub>2</sub> were carried out in a continuous flow, fixed bed glass reactor. The catalyst powder of 0.9 g was supported between glass wool plugs in a glass reactor which was placed in an electric furnace. The catalytic activity was determined using a feed gas composition of 5% CO and 5% O<sub>2</sub> in nitrogen. All these three gases were first mixed in a mixing bulb. The individual gas flow rates were controlled using flow meters and precision needle valves, previously calibrated for each specific gas. The mixture of gases was then allowed to pass over the catalyst at a rate of 5000 ml h<sup>-1</sup>. The temperature of the furnace was raised slowly from room temperature to the temperature at which 100% CO conversion is achieved. The feed gases and the products were analyzed employing an online Gas Chromatograph with molecular sieve 13X and Porapak Q columns. H<sub>2</sub> was used as a carrier gas. The CO was prepared in the laboratory by standard procedure and further purified by passing through alkali and molecular sieve traps. Oxygen, nitrogen and hydrogen gases were used from pure commercial cylinders.

The activity of the catalysts was tested for CO oxidation continuously for 5 h, by keeping the catalyst at a constant temperature. Also the effect of moisture on the catalytic activity was studied with low and high moisture contents at a fixed temperature.

## 3. Results and discussion

### 3.1. Characteristic properties

Fig. 1 shows the XRD pattern for MnO<sub>2</sub> and Mn<sub>0.92</sub>Pd<sub>0.08</sub>O<sub>2</sub>. The peaks were assigned for MnO<sub>2</sub> at the  $2\theta$  angles of 37.34° (1 3 1), 38.42° (2 3 0), 42.3° (3 0 0), 56.22° (1 6 0) and 65.04° (4 2 1) shown in Fig. 1a. All the reflections of the XRD patterns can be readily indexed to MnO<sub>2</sub> which agrees well with the values reported in literature (ICDD Card No. 14–0644). Whereas the XRD phase identification of Mn<sub>0.92</sub>Pd<sub>0.08</sub>O<sub>2</sub> revealed characteristic signals at

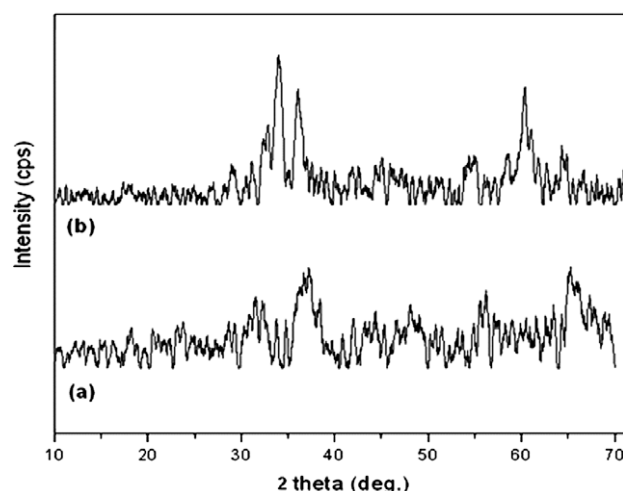


Fig. 1. XRD pattern of (a) MnO<sub>2</sub> and (b) Mn<sub>0.92</sub>Pd<sub>0.08</sub>O<sub>2</sub>.

$2\theta$  values of 34.04° (1 3 0), 36.04° (0 2 1), 55.03° (2 2 1) and 60.34° (2 3 1) which is shown in Fig. 1b and these reflections correspond to the ramsdellite structure of MnO<sub>2</sub> (ICDD Card No. 05–0600). Pd doped samples exhibits ramsdellite structure of MnO<sub>2</sub>.

The BET surface area of prepared samples is listed in Table 1. MnO<sub>2</sub> shows surface area 44 m<sup>2</sup>g<sup>-1</sup>. There is no decrease in surface area when palladium is doped in MnO<sub>2</sub>.

The surface morphology of the prepared catalysts was investigated by SEM and is shown in Fig. 2. From the SEM images it is observed that the particles are nano sized and in the range of 30–50 nm. Preparation of catalysts by co-precipitation technique in dextrose solution may highly influence the particle size, also not much agglomeration of particles is seen. Due to the addition of dextrose solution during preparation, the precipitated mixture does not get settled easily and they remain suspended in the solution. As a result, the particles got separated thus resulting in ultra fine, spherical nanoparticles.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) of MnO<sub>2</sub> and Mn<sub>0.92</sub>Pd<sub>0.08</sub>O<sub>2</sub> were carried out. All the samples showed the initial weight loss at 80–120 °C region which is generally due to loss of adsorbed water [28]. The weight loss in the region 560–700 °C is attributed solely to the loss of oxygen and this weight loss is generally considered due to the transformation of MnO<sub>2</sub> to Mn<sub>2</sub>O<sub>3</sub> phase [29]. Further weight loss in the temperature range 880–1050 °C is due to the conversion of Mn<sub>2</sub>O<sub>3</sub> to Mn<sub>3</sub>O<sub>4</sub> phase.

### 3.2. Catalytic performance

Fig. 3 shows the catalytic performance for CO oxidation of the MnO<sub>2</sub> and Pd doped MnO<sub>2</sub> samples. From the figure it is clear that Pd doped catalysts show high activity for CO oxidation. It is observed that the light-off temperature ( $T_{50}$ ) of Pd doped MnO<sub>2</sub> catalysts are at a much lower temperature than that of MnO<sub>2</sub>

Table 1  
BET surface area and catalytic activity of the samples.

Sample	SA (m <sup>2</sup> g <sup>-1</sup> )	T <sub>50</sub> (°C)	T <sub>100</sub> (°C)
MnO <sub>2</sub>	44	130	200
Mn <sub>0.98</sub> Pd <sub>0.02</sub> O <sub>2</sub>	55	87	110
Mn <sub>0.95</sub> Pd <sub>0.05</sub> O <sub>2</sub>	48	76	115
Mn <sub>0.92</sub> Pd <sub>0.08</sub> O <sub>2</sub>	45	69	90

T<sub>50</sub> Temperature for 50% conversion for CO oxidation.

T<sub>100</sub> Temperature for 100% conversion for CO oxidation.

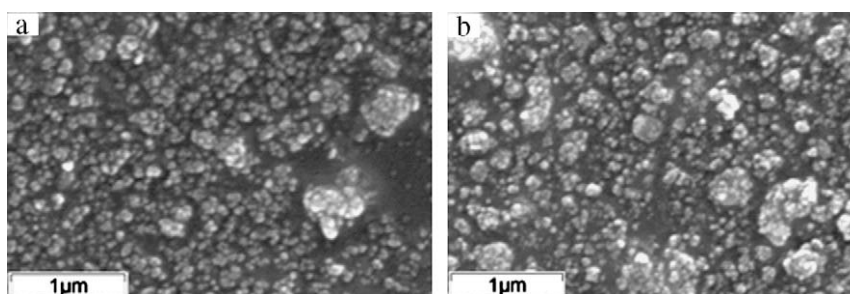


Fig. 2. SEM images of the catalysts: (a)  $\text{Mn}_{0.98}\text{Pd}_{0.02}\text{O}_2$  and (b)  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$ .

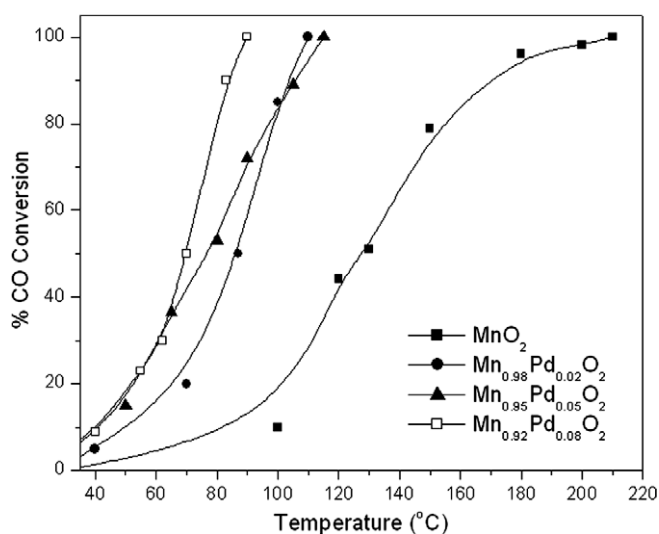


Fig. 3. CO conversion against catalyst temperature over different catalysts.

catalyst. The light-off temperatures of 50% CO conversion ( $T_{50}$ ) and 100% CO conversion ( $T_{100}$ ) over different catalysts are presented in Table 1. The addition of Pd in  $\text{MnO}_2$  facilitates the adsorption of CO as well  $\text{O}_2$  which in turn shows higher activity. The  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  gave total conversion at around 90 °C which is to a great extent much lower as compared to  $\text{MnO}_2$ , indicating that Pd doped  $\text{MnO}_2$  is an excellent catalyst for CO oxidation reaction.

Generally CO oxidation on transition metal oxides follows a mechanism proposed by Mars–Van Krevelen [30], implying that the lattice oxygen incorporation occurs during CO oxidation and that the reduced surface of the metal oxide is rejuvenated by taking up oxygen from the feed mixture [31]. On the other hand, it is well known that the reactivity for the structure sensitive reaction depends on the particle size, surface morphology and crystal plane of the catalyst [1]. Thus surface structure of the catalyst also influences catalytic performance.

Maximum CO conversion over metal oxide catalyst greatly depends on the method of preparation. The surface area largely depends on the preparative methods and higher the surface area generally corresponds to higher oxidation activity. In spite of  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  having lower surface area it showed highest activity because Pd– $\text{MnO}_2$  interaction might have resulted into more active sites per unit surface area compared to other catalysts. It is seen that by introducing Pd in  $\text{MnO}_2$  influences the activity of  $\text{MnO}_2$  and 100% CO conversion is obtained at temperature of 90 °C, this gives evidence that by introducing Pd in  $\text{MnO}_2$  produces a strong Pd– $\text{MnO}_2$  interaction which may be similar like the interaction in Ag– $\text{MnO}_2$  [1] and this interaction results in more favorable surface active sites which gives higher CO conversion at low temperature.

### 3.3. Activity test for the catalysts and effect of moisture on its activity

The activities of the catalysts  $\text{MnO}_2$  and  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  were tested for CO oxidation continuously for 5 h by maintaining the temperature of the catalyst near to its 50% CO conversion temperature ( $T_{50}$ ).

$\text{MnO}_2$  catalyst was maintained at a fixed temperature of 130 °C to check the activity. Around 50% CO conversion was observed in 1 h. After 5 h nearly 55% CO conversion is observed, indicating increase in activity with time. Fig. 4a depicts the results of the activity test. No decrease in activity of the catalyst was accounted during this period, signifying that  $\text{MnO}_2$  catalyst is a good catalyst for CO conversion.

The activity of  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  was also tested for 5 h continuously. This test was performed to ascertain whether the activity of the catalyst retains with increasing reaction time or not. The catalyst was kept at a fixed temperature of 50 °C. With increase in the reaction time, the CO conversion remains almost constant with a slight increase. Fig. 5a shows the results of activity test. It was reported that palladium oxide powder shows high activity for CO oxidation even at room temperature [32], but its activity decreases with increasing temperature. But when  $\text{MnO}_2$  was doped with Pd, a strong interaction occurs between Pd and  $\text{MnO}_2$  which results in high catalytic activity. Even catalyst like Ag doped OMS-2 shows very low activity at 100 °C and its activity goes on decreasing with time [26].

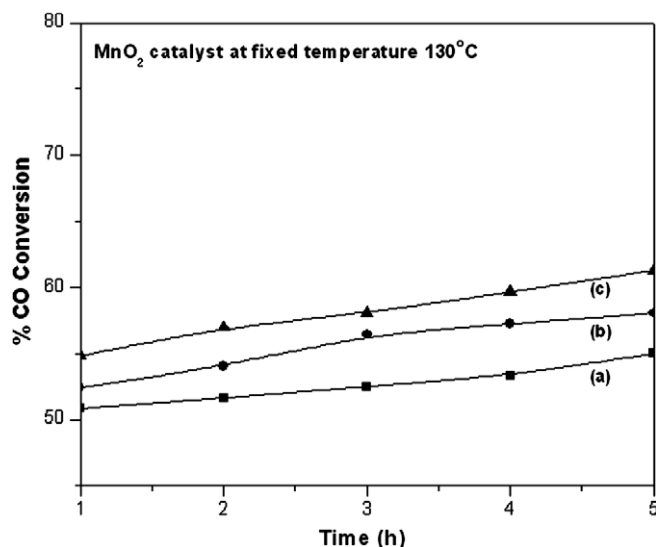
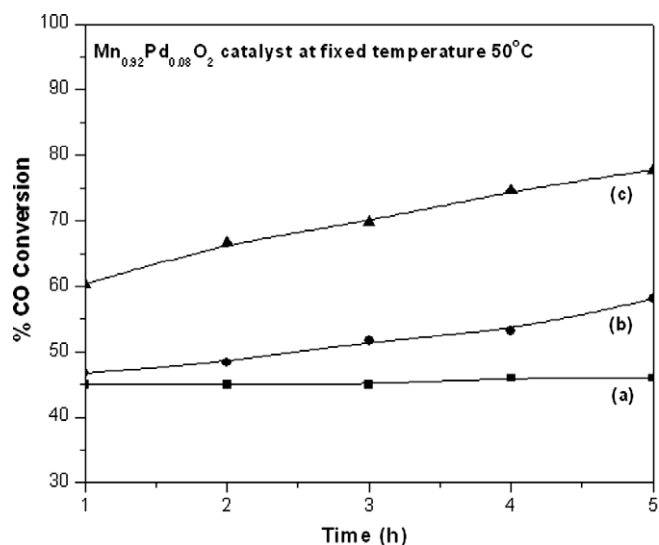


Fig. 4. Activity study of  $\text{MnO}_2$  catalyst at 130 °C for 5 h for CO conversion (a) activity without moisture, (b) effect of low moisture content on activity and (c) effect of high moisture content on activity.



**Fig. 5.** Activity study of  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  catalyst at 50 °C for 5 h for CO conversion. (a) Activity without moisture, (b) effect of low moisture content on activity and (c) effect of high moisture content on activity.

The effect of moisture on the activities of  $\text{MnO}_2$  and  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  catalysts were tested. The activity was tested in the presence of low and high moisture content. The activity of the catalyst in the presence of low moisture content was tested by allowing the mixture of feed gases to pass through water trap (maintained at room temperature) before passing through the catalyst bed. At room temperature the number of water molecules passing along with feed gases is around  $1.6730 \times 10^{21}$  molecules  $\text{h}^{-1}$ . Also the activity of the catalyst was tested with high moisture content by allowing the mixture of feed gases to pass through water trap (maintained at 50 °C temperature) before passing through the catalyst, at 50 °C the number of water molecules passing along with feed gases is around  $8.3117 \times 10^{21}$  molecules  $\text{h}^{-1}$ . In both the studies catalyst temperature was kept constant and activity was tested for 5 h continuously.

$\text{MnO}_2$  catalyst was kept at a fixed temperature of 130 °C, and then the mixture of feed gases coming from the water trap was allowed to pass through the catalyst bed. Under the influence of low moisture, after 1 h, nearly 52% CO conversion was observed. Later CO conversion was found to increase and after 5 h 58% CO conversion was observed as seen in Fig. 4b. This illustrates that the catalyst retains its activity under the influence of moisture and the results obtained in presence of moisture are much better than in absence of moisture. With increasing time of the reaction there is an increase in activity of the catalyst indicating optimistic effect of moisture on the  $\text{MnO}_2$  catalyst. The effect of high moisture content on catalytic activity of  $\text{MnO}_2$  shows much better results as compared to low moisture content. More CO conversion was observed under the influence of higher moisture content. After 1 h, 55% CO conversion was observed and it goes on increasing with reaction time. Around 61% CO conversion was seen after 5 h, thus by providing more amount of moisture along with feed gases, the activity for CO conversion was seen to increase as shown in Fig. 4c.

The  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  catalyst was also tested to see the effect of moisture. The catalyst was kept at a fixed temperature of 50 °C. Under the influence of low moisture, after 1 h, 47% CO conversion was observed as shown in Fig. 5b and after 5 h it increases to about 58% showing increase in activity by roughly 10% after 5 h. The  $\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2$  shows excellent CO conversion activity with higher moisture content. Around 60% CO conversion was seen after 1 h and with increase in the time of reaction, it reaches to 78% after

5 h as seen in Fig. 5c. Consequently the activity of Pd doped  $\text{MnO}_2$  is also highly influenced by passing moisture along with the feed gases and with more moisture it gives much better result.

From these findings it is seen that the presence of moisture strongly influences the CO conversion activities over these catalysts. No deactivation is observed for CO oxidation reaction. Obviously, the reaction mechanism of CO oxidation by  $\text{O}_2$  over these catalysts under the influence of moisture is likely to be different. Due to hydration of the adsorbed CO molecule, the CO bond is weakened significantly, which facilitates its oxidation [33] and presence of Pd highly influence this activity. Also water may increase the acidic sites on the surface of the catalyst [34] enhancing CO adsorption thus leading to higher activity.

#### 4. Conclusions

The Pd doped  $\text{MnO}_2$  catalysts showed high activity for CO oxidation and complete conversion was achieved at a much lower temperature as compared to  $\text{MnO}_2$ . The XRD pattern confirmed the formation of  $\text{MnO}_2$  phase. SEM images shows that particles are nano sized and in the range of 30–50 nm. Thermal analysis gives evidence for the phase change of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  with increase in temperature. The activity test carried out at fixed temperature showed that the activity does not fall with time but show slight increase in the percentage conversions. The influence of moisture has enhanced the activity over these catalysts.

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